

PATENT SPECIFICATION

Inventor: ROBERT SMITH-JOHANNSEN

772,449

Date of Application and filing Complete Specification May 14, 1954.

No. 14199/54.

Complete Specification Published April 10, 1957.



Index at acceptance:—Classes 37, S6(A3B: C3: C4); and 95, A9A, B4X.

International Classification:—B05. C09d. H01c.

COMPLETE SPECIFICATION

Improvements in Heat-Resistant Electrically Conducting Coatings

We, CHEMELEX CORPORATION, a corporation organized and existing under the laws of the State of New Hampshire, United States of America, of 101, Carpenter Street, Keene, State of New Hampshire, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrically conductive compositions and more particularly to electrically conductive coatings composed of particles of electrically conductive material dispersed throughout very finely divided colloidal silica. The present invention also embraces a method of applying such a composition to a surface.

Generally, electrically conductive coatings or films consist of a conducting material dispersed throughout a non-conductive adhesive vehicle. The nature of the materials and the concentrations used determine the electrical conductivity of the resulting films. The films are subjected to high temperatures during operation and the operating temperatures that may be safely employed are necessarily limited by the nature of the vehicles in which the conducting particles are dispersed. For example, films formed of silicone resins with conducting material dispersed therein, when applied to a surface and dried, are limited to operating temperatures in the neighbourhood of 400° C. At higher temperatures these films develop hot spots and burn out and so lose all adhesion to the surfaces upon which they were deposited. Similarly, films employing sodium silicate as an adhesive vehicle, besides being very susceptible to moisture, fail when approaching red heat by the formation of hot spots resulting in spontaneous burn-out.

A coating composition according to the present invention comprises an aqueous dispersion of particles of electrically conductive material and an alkali-stabilized colloidal silica in the form of dispersed particles having a particle size of 1 to 100 millimicrons and having the

alkali substantially all outside the silica particles. Applied films of the composition of the present invention are extremely heat resistant in that they withstand operating temperatures of a much higher order than has been heretofore possible without burn-out or loss of adhesion. These films may be operated at extreme temperatures of greater than 600° C. The films have good hardness, abrasion resistance and bond strength. When the films are brought up to red heat by passing a current therethrough, they are unaffected and there is no decrease in the bond strength to the surface upon which they are applied. The compositions of the present invention produce highly conducting and highly reinforced paint films.

The compositions of this invention may be prepared in the form of an aqueous suspension, a fluid composition, or a paint, and marketed as such. These paints can be applied in any conventional manner such as by brushing, spraying, or dipping to various surfaces and dried. The compositions may be air dried or set by baking. It is an advantage of the compositions of this invention that they can easily be air dried. After the compositions have dried they adhere to the surface to which they were applied and the particles of electrically conducting material bond into electrically conductive paths together with the silica bonding agent in a porous structure as herein described. These coatings on various surfaces may be applied to the thickness desired.

The colloidal silica used according to this invention is marketed by E. I. DuPont de Nemours and Company under the name Ludox. The word Ludox is a registered trade mark. The exact composition of Ludox colloidal silica can be varied in many respects as is hereinafter pointed out. The most common Ludox colloidal silica marketed is generally composed of 29 to 31% SiO_2 , 0.29 to 0.39 Na_2O and with a maximum of 0.15% sulphates as Na_2SO_4 . The Ludox silica sol generally contains about 30% total solids with the remainder water. The silica particles in the more common Ludox silica marketed are

[Pric.

extremely small, ranging from about 0.01 to 0.03 microns.

Ludox colloidal silica is further characterized as a stable aqueous silica sol having a silica-alkali ratio of from about 60:1 to 130:1 based on Na_2O and containing discrete particles having a molecular weight, as determined by light scattering, of more than one half million. It has a relative viscosity at 10% SiO_2 and 90% water from 1.15 to 1.55 relative to water at 20° C. and generally contains from about 20 to 35% by weight of SiO_2 . The particles of Ludox are of colloid dimensions, that is, particles having an average size not exceeding 100 millimicrons (0.1 micron) nor less than about 1 millimicron (0.001 micron).

The silica-alkali ratio of Ludox silica calculated as Na_2O may also be as low as 10:1 but it is advantageous to use a Ludox silica containing a silica-alkali ratio of between about 60:1 to 130:1. The silica-alkali ratio makes it obvious that the silica and alkali are combined in a special manner not found in conventional metal alkali silicates since the latter cannot be prepared in a form soluble and stable in aqueous solutions at ratios above 4:1. The alkali present is not uniformly distributed throughout the SiO_2 particles as it is in conventional silicate such as water glass but is substantially all outside the SiO_2 particles. The alkali is present as a stabilizer for the SiO_2 sol and prevents condensation of the SiO_2 particles. The Ludox silica sols could be prepared and used in the absence of alkali but this is not practical because they gel up very rapidly and cannot be stored.

Ludox colloidal silicas are generally prepared by passing a silicate through an ion exchange resin to remove the alkali as described in United States Patent No. 2,244,325. If all of the alkali is removed from the silicate, the resulting sols are not stable, but they can be stabilized by adding a small amount of alkali such as Na_2O or K_2O .

It is also particularly advantageous to use colloidal silica having a particle size of less than about 30 millimicrons (0.03 micron). The particle size of Ludox colloidal silica is determined as the average size of particle present when the solution is diluted to about 0.1% SiO_2 with water and dried in a very thin layer deposit.

It is also advantageous to use a Ludox silica containing between about 29—30% SiO_2 although higher and lower amounts can be used. Stable Ludox silica sols containing 5 to 15% SiO_2 can be prepared according to the United States Patent No. 2,244,325, while the more advantageous Ludox silica sols containing 20 to 35% by weight SiO_2 can be prepared according to the United States Patent No. 2,574,902.

In practicing the invention the colloidal silica is mixed with electrically conductive particles of a much larger size than the silica particles

and formed into a slurry. The conductive particles may range in size from about 0.1 microns up to about 20 mesh. Where graphite powder is used, it may be employed in a particle size range of from about 1 to 10 microns. A typical example of a composition of the present invention in parts by weight is as follows:—

Colloidal silica "Ludox" 75 (30% solids)
Fine graphite powder - 25

Water is used as the dispersing medium and it is only necessary to add sufficient water to form a coatable composition. The extremely active particles of the colloidal silica act as a very strong binder in themselves, and it is not necessary to use any soluble binder at all with the above composition.

Films of the composition of the invention applied to surfaces, such as insulating surfaces, have excellent electric conductivity and physical properties. The films have good hardness, abrasion resistance and bond strength and these properties are unchanged by heating the film to red heat. The watt density may be raised up to about 20 watts per square inch without any arcing or burnout. Even under severe conditions when the watt density is raised to where severe arcing and burn-out does occur, there is no observable decrease in the bond strength to the surface upon which the film is deposited. The films give off no objectionable odors during heating. The films have good heat aging properties, and stable electrical properties, so that the resistance does not change during use.

The proportions of electrically conductive material which may be dispersed throughout the colloidal silica slurry may vary within wide limits. For example, when graphite is present in amount of about 60% or less based on the total solid content of the silica and graphite in the mixture, good electrical conductivity and physical properties result. When the graphite percentage is reduced to about 25% and below, the conductivity of the composition falls off rapidly. A preferred range is about 29% to about 51% graphite. These limitations, however, are not to be considered critical, for the graphite concentrations may fall outside these limits dependent upon the degree of conductivity desired in the film and the presence of other materials in the mixture in addition to the graphite and colloidal silica. It is desirable, however, to have a surface resistance of between 10 and 100 ohms per square and the concentrations of the electrically conductive material should be sufficient to obtain a resistance within that range. The nature of the electrically conductive material chosen will also effect the electrical conductivity of the resulting films and also the proportions of electrically conductive material which will be necessary to achieve the desired electrical conductivity.

Many electrically conductive materials suitable for use in electrically conductive films may be utilized with the colloidal silica accord-

ing to the present invention. Examples of suitable electrically conductive materials are colloidal or semi-colloidal graphite, finely divided graphite powder, graphite flakes, colloidal carbon, and the like. These electrically conductive materials may be used singly or in combination. A combination of a finely divided powdered material with a material of larger particle size is advantageous. Flakes are particularly effective as the larger particle size conductive material. A combination of finely divided graphite powder with graphite flakes has been found to be particularly advantageous. Other combinations may, of course, be employed.

Combination of large and small electrically conductive materials prevent crack formations and permit high loadings and thus less resistance in the dried film.

It is also possible to impregnate applied films composed of the composition of the present invention with solutions of various resinous materials. The impregnation of the films still further increases the film strength and adds surface insulation without raising the resistance of the films more than a few per cent. The impregnation by a resin solution does not disrupt the electrical conductivity paths established during the initial drying.

A wide variety of resinous materials may be used for impregnating the films. Various natural or synthetic resins commonly used in protective coatings or paints such as phenolic resins, alkyd resins, thermoplastic vinyl resins and the like may be utilized, if desired. However, silicone resins are particularly effective. Silicone resins containing alkyl or aryl groups, or both, such as polymethylsilicones, dimethylsilicones, diethylsilicones, methylethylsilicones, phenylsilicones, methylphenylsilicones and the like may be utilized. Blends of the above may, of course, be used, if desired. The choice of resin depends largely on the desired flexibility of the film and the operating temperatures desired.

The films when impregnated with solutions of organic or silicone polymers will, of course, have an operating temperature limited to the operating temperature of the particular resin used to impregnate the electrically conductive colloidal silica film. Such films are useful in a moderate temperature range. The films made in this manner by impregnating the dried conductive colloidal silica films are far stronger and tougher than films of equivalent electrical properties made by dispersing the conductive colloidal silica mixture directly in the resin. As hereinbefore pointed out, conductive films formed with the irreversibly precipitable colloidal silica cannot be redispersed. Thus, impregnating such films with any resinous material dissolved in a suitable solvent does not affect the very strong and tough bond between the particles of the electrically conductive material or disrupt the electrical conducting paths established during the initial drying

which constitute the electrical circuit. The bond is thus not infiltrated or weakened by the resin or solvent.

The watt densities of the films formed from the composition of the present invention can be raised to values above about 20 watts per square inch by adding low melting (650—1000° C.) metal oxides to the composition while maintaining the conductivity between 10 and 100 ohms per square. The addition of clay, mica dust, calcium carbonate and zinc dust, either alone or combined and in amounts totaling up to about 25% by weight of the composition, causes a reduction in the arcing and burn-outs. Clay is particularly effective and can be usefully incorporated in proportions of from about 12% to about 48% by weight where the remaining ingredients are colloidal silica and graphite. The addition of low melting metal oxides such as antimony oxide (Sb_2O_3) and bismuth oxide (Bi_2O_3) in proportions within the same range quite effectively prevents arcing. Antimony oxide and bismuth oxide are particularly advantageous in this respect and are even more effective when combined than when used separately.

An example of a composition embodying the addition of clay is as follows, the proportions being in parts by weight:—

Colloidal silica "Ludox"	59 (30% solids)
Fine graphite powder	19
China clay	22

Total 100

An example of a composition embodying the metal oxide addition is as follows, the proportions being in parts by weight:—

Colloidal silica "Ludox"	59 (30% solids)
Fine graphite powder	19
Antimony oxide	11
Bismuth oxide	11

Total 100

When an asbestos board is coated with the above formulation and fitted with appropriate electrodes, it is possible to operate at a watt density of 20 watts per square inch for a considerable length of time without failure occurring.

What we claim is:—

1. A composition comprising an aqueous dispersion of particles of electrically conductive material and an alkali-stabilized colloidal silica in the form of dispersed particles having a particle size of 1 to 100 millimicrons and having the alkali substantially all outside the silica particles.

2. The composition according to Claim 1, in which the electrically conductive material is graphite.

3. The composition of Claims 1 and 2 in which the particle size of the silica particles is less than 30 millimicrons.

4. The composition according to Claims 2 and 3 in which the silica-alkali ratio is between

- 60:1 and 130:1 and the average molecular weight, as determined by light scattering is more than one half million.
5. A porous electrically conducting composition comprising particles of electrically conducting material distributed throughout and bonded together with colloidal silica particles having a particle size of 1 to 100 millimicrons and having substantially no alkali distributed throughout the silica particles.
6. Porous electrically conducting compositions according to Claim 1 in which the electrically conducting material is graphite.
7. Porous electrically conducting compositions according to Claims 6 and 7 in which the particle size of the silica particles is less than 30 millimicrons.
8. Porous electrically conducting compositions according to Claims 6 and 7 in which the silica particles have an average molecular weight, as determined by light scattering, of more than one half million.
9. Electrically conducting compositions according to Claims 6 to 8 in which the pores are filled with a resinous material.
10. Electrically conducting composition of Claims 6 through 9 which are adhered to a surface.
11. The method of coating a surface with a porous electrically conductive composition which comprises applying to the surface a composition comprising particles of graphite dispersed throughout an aqueous alkali-stabilized silica in the form of dispersed particles having a particle size of 1 to 100 millimicrons and in which the alkali is substantially all outside the silica particles and allowing the composition to dry and adhere to the surface.
12. The method of coating a surface with a porous electrically conductive composition according to Claim 11 in which the silica particles have a size of less than 30 millimicrons, in which the silica-alkali ratio is from about 60:1 to 130:1, and in which the silica particles have an average molecular weight, as determined by light scattering, of more than one half million.
13. The method of coating a surface with a porous electrically conductive composition according to Claims 11 and 12 in which the pores of the dried porous electrically conducting coating are filled with a resinous material.
- CRUIKSHANK & FAIRWEATHER,
29, Southampton Buildings, Chancery Lane,
London, W.C.2, and
29, St. Vincent Place, Glasgow,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1957.
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.